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An XPS study of intensity borrowing in core ionization of free and coordinated CO

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It is shown experimentally that the pronounced satellite peaks (shakeup) seen in the core level spectra of transition metal carbonyls borrows intensity from the main line. The core level spectra of free uncoordinated molecules like CO, N₂, O₂, NO, and CO₂ and transition metal carbonyls like Fe(CO)₅ can be understood using simple intensity sum rules based on the sudden approximation. By applications of the "Manne-Aberg theorem," we are able to explain binding energy shifts that occur upon coordination of a molecule as effects due to relaxation in the ion rather than to initial state shifts. The importance of the shakeoff continuum is addressed. Finally, a comparison of the satellite energies and positions is made to the excitation spectra of the neutral molecule. A CNDO/2-CI calculation is used to support the conclusions based upon this comparison.

I. INTRODUCTION

The pronounced satellite structure (shakeup and shake-off) accompanying the core ionization of transition metal carbonyl complexes has gained increasing interest since it has been shown that these molecules can serve as model systems for surface studies.¹⁻⁴ The two spectra in Fig. 1 show these satellite peaks for the photoionization spectra from the O_{1s} core level of CO, coordinated to a multimetal complex. There is intense shakeup structure starting about 5 eV below the main ionization line and extending for about 30 eV. The positions and intensities of the peaks in the spectra shown in Fig. 1 are determined by the ionization process. Therefore, the binding energies are not directly related to the states of the neutral system, and cannot be used in a straightforward way to deduce information on the charge distribution in the ground state of the system.⁵ We will show experimentally that by using the sum rules deduced from the sudden approximation the true initial state "chemical shift" can be measured.

Experimentally we find that the intense satellite lines in the carbonyl spectra shown in Fig. 1 have stolen intensity from the main line when compared to the spectrum of free CO. The concept of intensity borrowing is based upon the sudden approximation.⁶ In this model of photoionization the removal of the electron is assumed to occur so rapidly that the remaining $N - 1$ electrons are frozen. This frozen $N - 1$ particle state is not an eigenstate of the $N - 1$ ionic potential, but a superposition of all possible ion states ψ_{ij}^{N-1} including both single hole, particle hole states, and hole-continuum states. Each of these ionic states ψ_{ij}^{N-1} can have a different energy resulting in a multitude of satellite lines. The consequences of the sudden approximation can be more easily visualized if we write down the initial and final wave functions that will be used to calculate the photoionization intensity I , in the dipole approximation

$$I_{if} \propto |\langle \psi_{\text{final}} | \mathbf{P} | \psi_{\text{initial}} \rangle|^2. \quad (1)$$

The initial state is described by^{7,8}

$$\psi_{\text{initial}} = |\phi_j\rangle |\psi_j^R\rangle, \quad (2)$$

where ϕ_j is a one-electron state for the electron that is to be removed and $\gamma \Psi_j^R \gamma$ is the properly antisymmetrized $N - 1$ particle determinant to represent the rest of the electrons in the neutral system. The final state can be written as⁸

$$\psi_{\text{final}} = |u_k\rangle |\psi_{ij}^{N-1}\rangle, \quad (3)$$

where u_k describes the emitted electron (momentum k) which is supposed to be uncorrelated with the ion. ψ_{ij}^{N-1} describes all ionic states with a hole in the j th shell. The i is an index to identify these ionic states. Figure 2 shows a pictorial representation of the labeling on Ψ_{ij}^{N-1} . The first column is for the neutral ground state, (00). (04) describes the ground state of the $(N - 1)$ electron system. (01) is the excited hole state corresponding to a core ionization, while (11) is an example of a particle-hole state responsible for the shakeup satellite.

The intensity in each satellite line can be calculated with the sudden approximation using Eqs. (1)-(3):

$$I(i, f) \propto |\langle u_k | \mathbf{P} | \phi_j \rangle \langle \psi_{ij}^{N-1} | \psi_j^R \rangle|^2. \quad (4)$$

Since the functions Ψ_{ij}^{N-1} form a complete set the sum over all excited states i gives⁹

$$\sum_{i=0}^{\infty} |\langle \psi_{ij}^{N-1} | \psi_j^R \rangle|^2 = 1. \quad (5)$$

Equations (4) and (5) have a simple interpretation. The cross section for ionizing from a core hole in an atom is constant independent of the environment of the atom, and is given by the square of the first term in Eq. (4). The intensity is spread out over all of the possible ionic states ψ_{ij}^{N-1} , implying that a given peak can change intensity only by "borrowing" from other peaks. Figure 1 already illustrated that CO molecules bound to a transition metal in a carbonyl have intense satellite lines in the core level spectra. These satellite or shakeup lines must have borrowed intensity from the main

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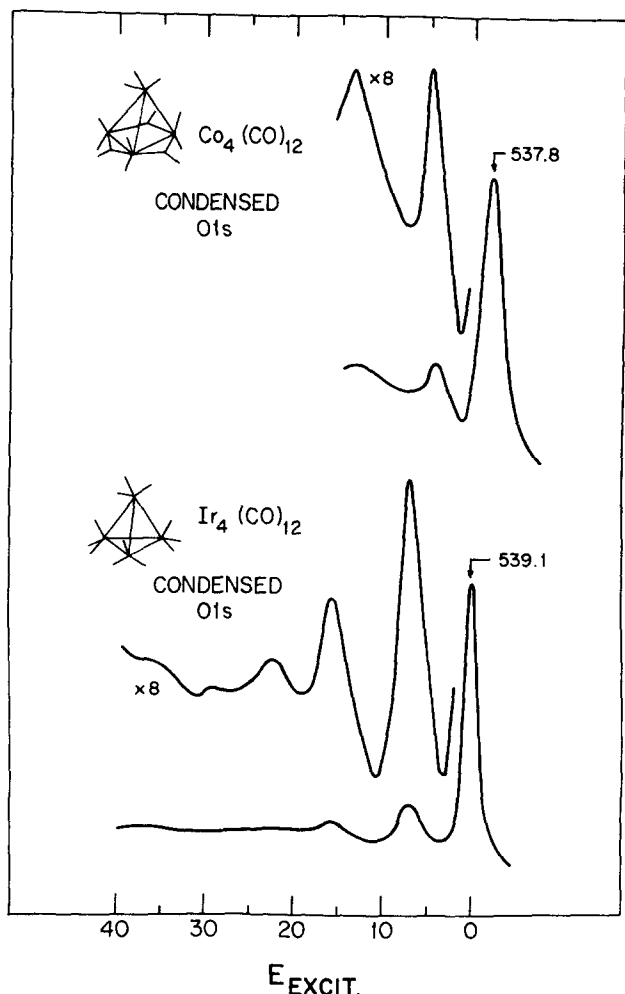


FIG. 1. O_{1s} core hole spectra of tetrametal-dodecacarbonyls as examples of intense satellite peaks in CO-coordinated systems (MgK_{α} excitation).

line, compared to free CO. This sum rule must include the sum over the continuum states.

Manne and Aberg⁹ showed that the binding energies of the ionic states E_{ij}^{N-1} can be incorporated in the form of another sum rule. This rule connects the ionization energy derived from Koopman's theorem $-E_j^{\text{rozen}}$ with the sum of intensity I_{ij} of each peak in the spectrum weighted by the excitation energy $E_{ij}^{\text{ion}} - E_{0j}^{\text{ion}}$ of the ion, with the same hole state j .

$$-E_j^{\text{rozen}} - E_{0j}^{\text{ion}} = \sum_{\substack{i=0 \\ \text{bound} \\ \text{states}}} I_{ij} (E_{ij}^{\text{ion}} - E_{0j}^{\text{ion}}) + \int_{\text{continuum}} I_j(E) E dE, \quad (6)$$

the energy difference on the left-hand side is called the relaxation energy (E_R) and accounts for the reorganization and correlation energy difference of the electrons upon creation of the core hole.⁵ The contribution of the excitations to the relaxation energy (E_R) can be split up into those from bound states and continuum excitations.¹⁰ The continuum excitations (called shakeoff) have energies between 25–40 eV¹¹ for the systems under consideration in this paper. It is clear from Eq. (6), that even weak transitions of this excitation energy contribute con-

siderably to the sum. The importance of the shakeoff continuum for the determination of relaxation energies¹² will be quantified in the course of this paper.

We have investigated the applicability of the sum rules [Eqs. (5) and (6)] for six different molecules: CO, O_2 , N_2 , CO_2 , and $Fe(CO)_5$.

II. EXPERIMENTAL

The experiments were performed in an AEI-ES-200B photoelectron spectrometer, equipped with a gas cell. A capacitance manometer (MKS-Baratron-222) was incorporated into the gas handling system attached to the cell. This configuration allowed absolute pressure measurements. Pressure variations were kept below 1%. The vapor pressure of the $Fe(CO)_5$ carbonyl compound was sufficient to take the full spectrum (50 eV scan) of the O_{1s} ionization without heating above room temperature. Since $Fe(CO)_5$ decomposes easily which eventually leads to a deposition of iron on the x-ray window and consequently to a time dependent decrease in signal, the intensity was always referenced to intermediate scans with CO gas.

In order to assure that characteristic losses did not contribute to the observed intensity, the spectra were taken when the intensity was a linear function of pressure. In this case, the known 1π characteristic loss at 11 eV¹³ excitation energy (relative to the main line) in CO, for example, was no longer detectable. Figure 3 shows the O_{1s} spectra of CO and $Fe(CO)_5$ at the same pressure, Fig. 4 displays the core spectra for all of the other small molecules which are used for comparison with CO in this paper. Table I compiles intensity ratios relative to the main ionization line for all of the molecules studied. Column I gives the measured intensities relative to the O_{1s} ionization. Column II gives the difference (in percent) between column I and an intensity that is expected if the number of atoms in the molecule determined the intensity ratio. If the measured intensity is smaller than the expected intensity the sign is negative. Column III contains the shakeup intensities relative to the main lines. Column IV gives the relative total intensity including satellites. For O_{1s} , C_{1s} , and N_{1s} , a reference molecule is chosen and its total intensity was set equal to unity. In column V, the values from column IV have been divided by the number of equivalent atoms in the molecule. Finally, column VI gives the same information as column II, but for the total integrated intensities.

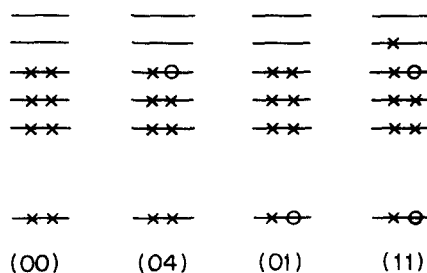


FIG. 2. Schematic one-electron representation of electronic states in the neutral molecule and the corresponding ion.

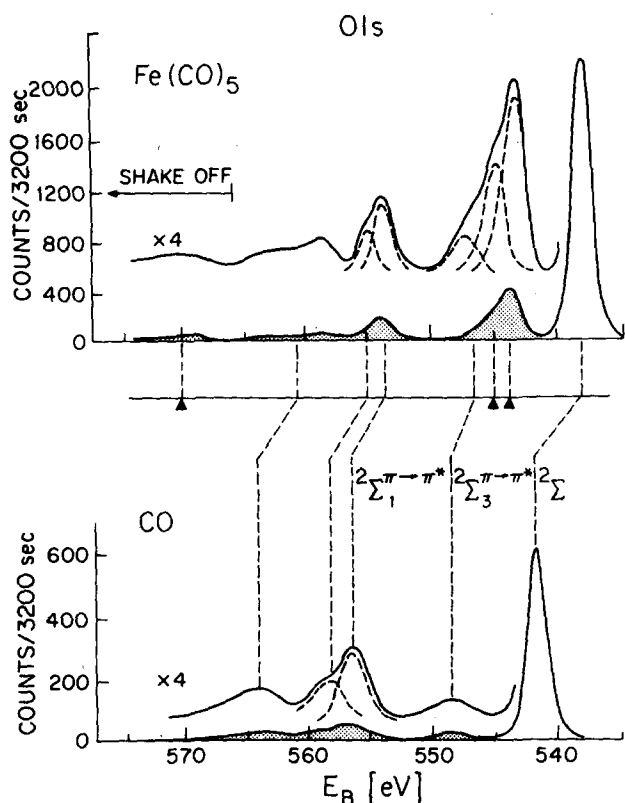


FIG. 3. O_{1s} core hole spectra of gaseous $Fe(CO)_5$ and CO taken at the same pressure in the gas cell (MgK_{α} excitation).

III. RESULTS AND DISCUSSIONS

A. Small molecules and comparison to atoms

1. Intensities and relaxation energies

In this section, we analyze the $1s$ core ionization spectra of N_2 , CO, NO, and O_2 ¹⁴⁻¹⁹ with emphasis on two issues: one is the partitioning of the satellite intensities with respect to shakeup and shakeoff processes, the other one, which is intimately connected with the first one, is the determination of relaxation energies from experimental data.

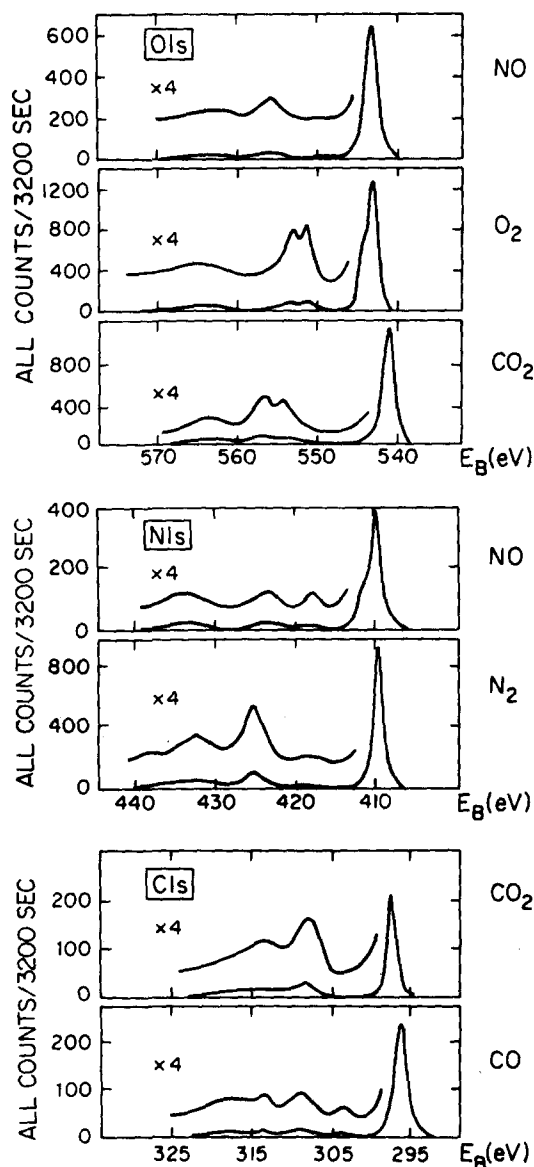


FIG. 4. O_{1s} , N_{1s} , and C_{1s} core hole spectra of NO ¹⁴, O_2 ,¹⁵ CO_2 ,^{15,16} CO ^{13,15} at the same pressure within the gas cell (MgK_{α} excitation).

TABLE I. Intensities of core level peaks.

Ionization	Molecule	I	II	III	IV	V	VI
		Main line relative	Intensity loss/atom (main line)	Satellite intensity relative to main line	Integrated intensity relative	Integrated intensity per atom	Intensity loss/atom
O_{1s}	CO	1.000		0.265	1.000	1.000	0.0
	CO_2	1.833	-8.35%	0.270	1.840	0.92	-8%
	O_2	1.980	-1.00%	0.22	1.91	0.96	-4%
	NO	1.007	+0.70%	0.22	0.971	0.97	-3%
	$Fe(CO)_5$	3.585	-28.3%	0.64	4.65	0.93	-7%
C_{1s}	CO	0.344		0.21	1.000	1.000	0.0
	CO_2	0.322	-6.4%	0.23	0.951	0.951	-5%
	$Fe(CO)_5$	1.180	-31.3%				
N_{1s}	N_2	1.159	-12.46%	0.29	1.87	0.94	-6%
	NO	0.662		0.21	1.000	1.000	0.0

TABLE II. Threshold energies for shakeoff processes. Energies in (eV).

Molecule	O _{1s}	C _{1s}	N _{1s}
O ₂ ^a	37.4		
N ₂ ^a			42.9
CO ^a	40.2	39.9	
NO ^a	34.7		35.7
CO ₂ ^a	37.4		
Cr(CO) ₆ ^b	27.2		
Mo(CO) ₆ ^b	28.9		
W(CO) ₆ ^b	27.7		
C ₃ O ₂ ^c	29.9	29.5 26.1	

^aReference 11.^bReference 2.^cReferences 17 and 18.

In order to separate the satellites of a 1s ionization into shakeup and shakeoff contributions you have to determine the minimal energy necessary to create a double ion with the primary hole in the 1s shell. This energy is given by the difference between the kinetic energy of the lowest energy KLL–Auger transition and the binding energy of the 1s ionization. For the molecules studied here these values are collected in Table II. For two- and three atom molecules the values range between 34 and 43 eV, depending basically on the energy of the highest occupied orbital of the molecule under consideration. The photoelectron spectra of N₂, CO, NO, CO₂, and O₂ in Figs. 3 and 4 show that the measured satellite structure is well below the shakeoff threshold. Experimentally the electron shakeoff intensity is extremely difficult to measure since the shakeoff excitations produce a weak, broad and continuous background. The experimental information presented here is, however, sufficient to compare the total intensities of free and coordinated CO. The only assumption we have to make is that the total shakeoff intensity for a given core level is constant. We will show that this is reasonable within certain limits, i. e., 5% of the total intensity:

It is generally accepted that the cross section of a core ionization is independent of the molecular environment and reflects the number of each atomic species. This is true of course only for the total integrated intensity including main line, shakeup and shakeoff satellites. Column V in Table I shows the experimental sum of the main line and shakeup intensity per atom. These data in column V show that the intensity in the sum of the main line and shakeup reflects the number of atoms within ~5%, without the inclusion of the shakeoff intensity. Therefore, the percent of the total intensity in the shakeoff must be constant, independent of the environment. This is most dramatic for the carbonyl, where ~30% of the main line intensity is missing.

Knowing that the shakeoff intensity is basically constant we now turn to the analysis of relaxation energies defined by Eq. (6). First we consider the atomic case:

neon. The relaxation energy of neon has been calculated to be 24.8 eV.¹³ Neon is one of the few cases where the shakeoff intensity has explicitly been measured. So we can integrate the spectrum and determine an experimental value for the relaxation energy. Using the spectrum of Carlson *et al.*^{20,21} (Fig. 2 in Ref. 20) we get by numerical integration, a shakeoff contribution of 14.4 eV. The shakeup contribution can be evaluated from Gelius' results on neon¹³ to be 6.2 eV, which adds up to 20.6 eV, being 83% of the calculated relaxation energy. According to Meldner and Perez¹² two and three electron shakeoff contributions have to be included leading to an additional contribution of 4.8 eV. Including all processes, we reach 25.4 eV for the experimental relaxation energy compared to 24.8 eV¹³ calculated. This analysis exemplifies the important role of continuum excitations for the determination of relaxation energies. In going from Ne_{1s} to the C_{1s} ionization the atomic relaxation energy drops from 24.8 eV for Ne¹³ to 13.7 eV¹³ in atomic carbon. Hedin and Johansson²² pointed out, that by decreasing the atomic number (*Z*), the outer valence electrons become less screened and, thereby, experience a smaller perturbation by the removal of a core electron, which then leads to a smaller relaxation energy. Table III collects calculated and empirically deduced relaxation energies. Remarkably the relaxation energies of a given atom are basically the same, independent of the molecular system. Note that carbon, nitrogen, and oxygen have open shell configurations leading to a manifold of states. Each state is connected with a different relaxation energy as has been demonstrated by Bagus *et al.*²³ For oxygen and nitrogen two relaxation energies are given, depending upon which final ionic state is chosen. For carbon the values for different spin states are not available. The given relaxa-

TABLE III. Relaxation energies in (eV).

Species	C	N	O	Ne
C	13.7 ^a			
N		16.6 ^b		
O			19.9 ^a 18.03(<i>p</i> ⁴) 16.22(<i>p</i> ²)	
Ne				24.8 ^a
CO	10.79 ^b		19.91 ^b	
N ₂		16.4 ^c		
NO		16.7 ^c 16.61 ^c	20.78 ^c 4.05 ^c	
O ₂			21.3 ^c 21.49 ^b 22.38 ^c 22.56 ^b	
C ₃ O ₂ ^f	15.81 ^d 12.41 ^d		22.49 ^d	
Ni(CO) ₄ ^f	14.2 ^e		23.1 ^e	

^aReference 10.^bReference 23.^cReference 24.^dReference 18.^eReference 25.^fRelaxation energy taken from experiment.

TABLE IV. Charge densities in the neutral ground state and in the primary hole state for O_{1s} and C_{1s} ionization of CO.

Carbon monoxide				
	C	Δg	O	Δg
(NO)*	4.2568	-1.4706	5.7432	0.4706
*CO	2.7862		6.2138	
CO	3.7862	0.0	6.2138	0.0
CO*	3.7862		5.2138	
(CF)*	3.1125	0.6736	6.8875	-1.6737

tion energy is calculated for a spin-averaged state.²⁶ Therefore the atomic and molecular relaxation energies for a C_{1s} ionization cannot be compared directly. Summarizing, we see that the molecular relaxation energy is dominated by the atomic contribution which in turn supports the assumption of a constant shakeoff contribution.

We have tried to substantiate our analysis by theoretical calculations on CO and N_2 and their corresponding hole states. The calculations were done using the CNDO/S-CI approximation.²⁷ In order to calculate the hole states we use the equivalent-core approximation,²⁸ e.g., NO^+ to describe the C_{1s} ionization in CO and the N_{1s} ionization in N_2 , and CF^+ for the O_{1s} ionization in CO. The intensity of the main line is then given by the square of the projection of the lowest CO^+ -equivalent core state onto the ground state of the neutral system. Appendix A gives the overlap between determinants and, in addition, the individual contributions from each orbital. The main line intensities systematically vary from carbon to nitrogen to oxygen. Since the CNDO calculations do not contain a basis sufficient to describe excitations into the continuum the calculations only contain information on shakeup intensities.

Following our previous argumentation, we do not expect the shakeoff to vary considerably, which allows us to use these calculations as a guide. Although the total shakeup intensities are too small we find that for C_{1s} ionization the shakeup intensity is the smallest, for oxygen the biggest, and for nitrogen in between. The trend is easy to rationalize on the basis of charge distributions in the ion, which are given in Table IV in the case of CO and in Table V for N_2 . The tables are constructed in such a way that the unscreened hole is compared with the screened case, that is the self-consistently calculated hole state. The charge differences (Δg) given show that the hole charge is always overcompensated for by at

TABLE V. Charge densities in the neutral ground state and in the primary hole state for N_{1s} ionization of N_2 .

	N_1	Δg	N_2	Δg
N_2	5.000	0.0	5.000	0.0
N_2^*	4.000	-1.7432	5.000	0.7432
(NO)*	5.7432		4.268	

TABLE VI. Charge distributions in the primary hole states and in the $\pi^* - \pi$ excited ion states.

	C/ N_1	Δg	O/ N_2	Δg
CO	3.7862	0.4861	6.2138	-0.4861
CO (π, π^*)	4.2722		5.7278	
(CF)*	3.1125	0.8138	6.8875	-0.8138
(CF)* (π, π^*)	3.9264		6.0736	
(NO)*	4.2568	0.2960	5.7432	-0.2960
(NO)* (π, π^*)	4.5528		5.4472	
N_2	5.000	0.0	5.000	0.0
N_2 (π, π^*)	5.000		5.000	

least 0.5 electron. Consider for example, the C_{1s} ionization of CO. Table IV shows that the equivalent core molecule (NO)* has a valence charge of -4.2568 e around the C atom while neutral CO only has -3.7862 e. There is an overscreening of the C_{1s} hole by 0.47 e. This charge comes from the O end of the molecule.

In the case of CO, i.e., the O_{1s} hole is more effectively screened than the C_{1s} hole which in turn leads to stronger satellite structure for the O_{1s} than for the C_{1s} ionization of CO. We can proceed one step further and evaluate the $\pi^* - \pi$ and $\sigma^* - \sigma$ contributions to the total shakeup intensity. In the framework of our calculation this is easily achieved by calculating only the $\pi^* - \pi$ contributions since the rest is due to $\sigma^* - \sigma$ excitations in a minimal basis calculation. Those values are given in Appendix A. As expected the π -shakeup intensity increases in the same way as the total shakeup intensity. Table VI shows why this is the case. Table VI contains the charge distributions in those states, where the molecule is excited by a $\pi^* - \pi$ transition. In the case of CO, obviously, the $\pi^* - \pi$ excitation leads to a charge transfer from the oxygen to the carbon atom, regardless of whether there is a core hole. Clearly upon creation of a carbon hole, the charge transfer is smaller than in the neutral and even stronger upon creation of an O_{1s} hole. The reason for this behavior is simply that with the creation of a hole the two atoms become either more (C_{1s}) or less (O_{1s}) similar in electronegativity, which influences the balance of the wave function coefficients accordingly and leads to the calculated charge transfer. In other words, the stronger the charge transfer upon creation of the hole the stronger the shakeup.

2. Assignment of shakeup peaks at lower excitation energy of diatomic molecules

So far only a few calculations^{29,30} exist which are capable of assigning the core hole shakeup peaks. This is due to the importance of configuration mixing for the calculation of two-particle hole states.

We have chosen here an empirical approach to assign the shakeup peaks and try to connect the valence excitations in the neutral molecule with those accompanying the core ionization.^{11,31} Why this should be possible in the limiting case of low lying excitations can easily be seen: we use the highest occupied and lowest unoccupied

TABLE VII. Energy differences between occupied and unoccupied π orbitals.

Molecule	$\Delta E(\epsilon_{2\pi} - \epsilon_{1\pi})$ (eV)	$\Delta(\Delta E)$ (eV)
N ₂	19.94	4.59
(NO) ⁺	24.53	
CO	24.03	0.50
(CF) ⁺	26.75	2.72

orbitals of a diatomic (first row elements) as an example. Excluding configuration interaction, the excitation in the neutral molecule is given by the π -orbital energy differences corrected by Coulomb and exchange terms.³¹⁻³³ Upon creation of a core hole the screening of the electrons is altered. In principle, the altered potential influences occupied and unoccupied orbitals differently. The variations depend on the energy of the orbitals and on the shape of their wave functions. In the case of the π and π^* orbitals in a diatomic molecule, both molecular orbitals are linear combinations of $2p$ atomic orbitals. Therefore, we expect a similar response of the π and π^* orbitals upon creation of a core hole, which leads to the conclusion that the average excitation energy should be similar in the ion compared to the neutral system. If the binding energy of the unoccupied orbital increases, the difference in screening becomes more pronounced. In the case of an excitation into the continuum, the screening for the unoccupied orbital has changed by a full unit leading to the large threshold energies for a double ion (Table II), compared to the energy necessary to remove only one electron.

Support for these lines of thought is again gained from CNDO/S calculations²⁷ performed for the neutral ground states and the core hole states of CO and N₂ as described above. Table VII collects the 1π and 2π orbital energies for the neutral and the ionized species. The $\Delta(\Delta E)$ values given in the third column of Table VII demonstrate the applicability of the ideas outlined above.

Clearly this simple argument only allows us to rationalize the trends but not the detailed assignment of the individual states experimentally observed. In order to do this we have to include configuration interaction which is demonstrated by the following arguments: the $\pi^* - \pi$ excitation is fourfold degenerate (both singlet and triplet states) due to the degeneracy of the π orbitals in $D_{\infty h}$ or $C_{\infty v}$. The four degenerate excitations couple through configuration interaction³³ and get split by about 7 eV. Two of these states have $^+\Sigma_u$ spatial symmetry.³³ As you can see from Appendix B, $^+\Sigma_u$ states are the only states that can couple to the primary $1s$ -hole states. Therefore, only those states will have nonzero intensity [see Eq. (4)]. Appendix B allows us to correlate the excitations in the neutral molecule with those in the ion. Figure 5 shows a comparison of experimental excitation energies in the neutral molecule with those in the ion in the presence of a $1s$ core hole. The states of the neutral indicated in Fig. 5 by broken lines are those that by symmetry may couple to the primary hole state. The full lines represent the measured shakeup energies

(Figs. 3 and 4) with respect to the main line. The excitations in the neutral molecule are taken from optical and electron impact data.^{34,35} The bar indicates the excitation in the neutral with the lower multiplicity, i. e., the singlet $\pi^* - \pi$ excitation of the case of N₂. The biggest problem in this comparison is the lack of experimental information on higher excited states in the neutral molecule. We find that the agreement is rather good for the existing data: the trends for the various molecules are well reproduced. The splitting of the different spectroscopic states through configuration interaction is similar for the neutral and the ionic systems. The excitation energies themselves are at least in the correct energy range. We note that the states at higher excitation energy usually do not agree as well. This is expected from our qualitative arguments presented above.

We believe that based on a comparison between the neutral system and the ion it is possible to assign the lower energy range of shakeup satellites at least for these small molecules (see Fig. 3). For higher excited states the situation is not so simple. For the molecules investigated here, however, there are indications that the peaks observed in the spectrum are due to double excited $\pi^* - \pi$ transitions to $\sigma^* - \sigma$ and/or Rydberg transitions.^{29,30}

B. Coordinate CO; case study: Fe(CO)₅

1. Intensities and relaxation energies

We use the results on the free molecules to analyze the spectrum of Fe(CO)₅ as an example for the coordinated system.³⁶ As was pointed out we are limited to a comparison of the O_{1s} ionization. Figure 3 shows a direct comparison of the O_{1s} ionization in free CO and in Fe(CO)₅. The observed binding energy in Fe(CO)₅ is 3.3 eV smaller than in free CO. We will show that the difference is due to a difference in relaxation energy rather than to changes in the charge distribution of CO upon coordination. Table I shows the experimental evidence: Although there are five CO molecules in Fe(CO)₅ and you would expect a fivefold increase in the O_{1s} intensity compared to the free molecule, the main line is only larger by a factor of 3.6. This indicates a missing intensity of ~30% per atom (column II) in the main line, which is significantly more loss of intensity in the main line than in all other cases studied. If, however, all ob-

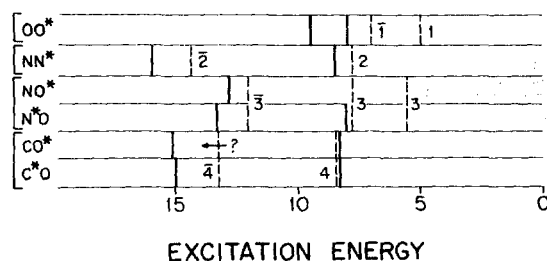


FIG. 5. Schematic comparison of energies of excited states of the neutral systems (dashed)^{34,35} and the core ionized ions (solid). All states indicated result from $\pi^* - \pi$ excitations. The energy of the higher excited state of CO(O_{1s}) is only a lower limit.

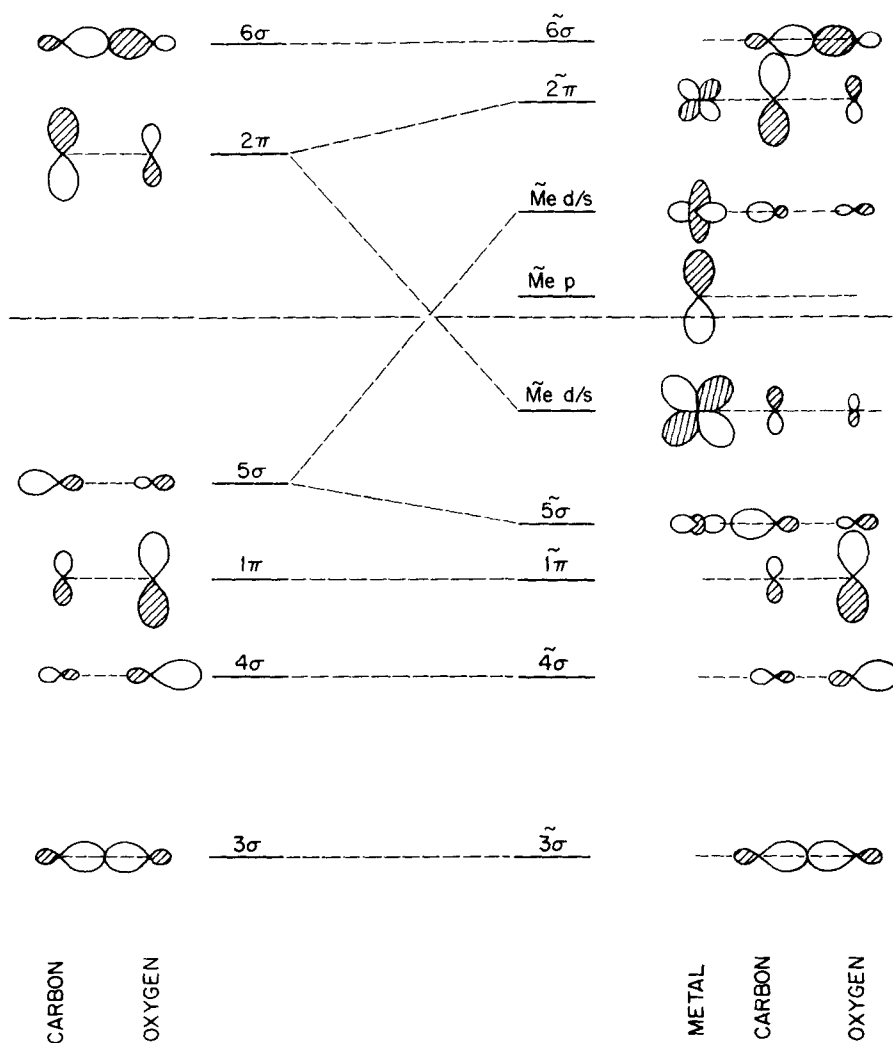


FIG. 6. Schematic correlation diagram of one electron levels in the free and coordinated CO molecule.

served satellite structure is included, the missing intensity is reduced to a level which is consistent with those deviations found for all molecules included in the comparison. These experimental results indicate that it is possible to understand the changes in terms of "intensity borrowing from the main ionization line." We can also calculate the center of gravity for the free CO molecule (546.4 eV) and the complex (546.09 eV), using the main line and shakeup peaks. This shows that the additional satellite intensity in $\text{Fe}(\text{CO})_5$ makes up for about 3.0 of the 3.3 eV binding energy difference. The binding energy difference is, therefore, $\sim 90\%$ due to a relaxation energy difference and only $\sim 10\%$ is due to an initial bonding energy shift. This result is in excellent agreement with the results of *ab initio*,³⁷ and X_α ,³⁸ and semi-empirical calculations^{3,39} on a variety of carbonyl compounds which all show only a small change in the charge distribution of CO upon coordination. The reason for the difference in relaxation energy is clear: upon creation of a core hole on the CO ligand, the metal electrons rush in to help screen the positive charge. We have discussed the screening mechanism for free and metal coordinated CO in detail elsewhere.⁵

So far we have not addressed another important ques-

tion: is the change in the satellite structure only due to changes in the shakeup or also in the shakeoff regime? First we note, that the integration of satellite intensities in the carbonyl has been extended over the same energy range of excitation energies as in the free molecules. Since the minimum energy for double ionizations decreases by about 10 eV upon coordination (Table II) the intensity integration includes that part of the shakeoff spectrum which lies above this excitation energy, while the intensity integration in the free molecule did not include any shakeoff contributions. At first this might seem to be inconsistent; a closer inspection of the Auger spectrum, however, reveals that the comparison is a reasonable one. Using the Auger data (O_{1s}) for $\text{Cr}(\text{CO})_6$ and CO reported by Plummer *et al.*,² one finds that the features belonging to hole states dominantly localized on oxygen atoms⁴⁰ are only shifted by 7 eV while those at lowest binding energy are shifted by approximately 13 eV. This indicated that the double hole states, which decrease the double ionization threshold in the coordinated system (Table II) are really new states. The double hole states localized on the CO molecules are still at high excitation energies not covered by our spectrum. It is therefore reasonable to integrate over the same energy range in the carbonyl

as in the free molecule.

In this connection we want to point out an analogy to carbon-suboxide (OCCO), which may be looked at as two CO molecules coordinated to a carbon atom. The rather intense shakeup peaks have been subject to several investigations.^{10,18,41-43} The main result we want to address here is that the relaxation energy as determined from the experimental spectrum¹⁸ is intermediate between the one for free CO and metal coordinated CO (Table III). This is consistent with the picture that the central carbon atom cannot provide as much screening charge as a transition metal atom.

2. Assignment of shakeup peaks at lower excitation energy

In order to assign the shakeup satellites in the carbonyl compound, we compare the spectrum of the free molecule with the spectrum of the complex. Figure 3 shows that we are able to account for part of the shakeup peaks of $\text{Fe}(\text{CO})_5$ by shifting the satellite peaks observed in the free molecule to lower binding energy. As we have pointed out in the last section, this energy contribution is a consequence of the additional screening of the core hole on CO by the metal electrons. We cannot expect, however, that the shift is the same for all peaks since the individual neutral ground state orbitals in CO are influenced differently by bonding of the CO molecule to the metal atom. Also, the configuration mixing that splits the spectroscopic states may be different in free and coordinated CO. Consider again the lowest lying shakeup states in free CO. According to the comparison in Fig. 3 the two final doublet states resulting from the $\pi^* - \pi$ excitation are shifted by 2.0 and 2.3 eV respectively, upon coordination. The splitting is altered by only 0.5 eV. The average energy of the excitation, therefore, increases by about 1.3 eV. This can be understood by assuming that the unoccupied 2π orbitals of CO are shifted to higher energy upon coordination. This assumption is in line with the conventional bonding scheme developed for CO complexes. Figure 6 shows a schematic representation of the wave functions. Because of the weight of the atomic coefficients on CO the orbital energy difference between 1π and 2π is influenced differently for C_{1s} and O_{1s} ionization. The 2π orbital on the other hand is destabilized by the interaction, leading to an increase of the energy difference between 1π and 2π orbitals relative to free CO. The increase of the average of 1.3 eV is in excellent agreement with our calculations on $\text{Fe}(\text{CO})_5$ using a modified CNDO method.³⁹

The broader structures at larger excitation energies are assigned in analogy to free CO. These excitations are shifted to lower energy as well in going from the free to the coordinated molecule.

The main shakeup features in the carbonyl which appear not to have an equivalent in free CO are the largest satellite at 5.8 eV excitation energy and the structure at slightly higher excitation energy (marked by triangles in Fig. 3). The latter structure has already been identified as shakeoff satellites through comparison with the energies in Table II. The peak at 5.8 eV is mainly due to electron transfer excitations, where an electron is transferred from a metal to a ligand level as we have discussed in detail elsewhere.⁵

Summarizing the presented argumentation leads to a natural explanation of the shakeup structure in carbonyls including the free molecule as a limiting case. It has been shown, that a similar assignment is possible for other carbonyl compounds (Fig. 1) and it can even be extended to CO adsorbates.⁵

IV. CONCLUSIONS

The main results of the present paper may be summarized as follows:

- We have shown, that the pronounced satellite structure in transition metal carbonyls borrows intensity from the main line.
- We can explain the change in binding energy of the carbonyl ionization relative to free CO by the difference in relaxation energy rather than a chemical shift in the initial state.
- We have demonstrated the importance of the shake-off continuum for the determination of the relaxation energy.
- We are able to assign the shakeup peaks of the free and coordinated molecules at lowest excitation energy by a comparison to the excitations in the neutral molecules. The limitations of this procedure are pointed out.

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APPENDIX A

TABLE AI. Overlap matrix between NO^+ and CO. Total shakeup intensity: $I_{\text{tot}} = 0.04$ (4%). $\pi^* - \pi$ shakeup intensity: $I_{\pi^* - \pi} = 0.01$ (1%). Those parts of the overlap matrixes constructed from occupied orbitals are enclosed by bold lines.

$\text{NO}^+ \backslash \text{CO}$	3σ	4σ	5σ	6σ	1π	2π
3σ	0.9925	0.1203	-0.0130	0.0150		
4σ	-0.1215	0.9754	0.1707	0.0670		
5σ	0.0083	-0.1678	0.9785	-0.0495		
6σ	-0.0065	0.0759	0.0380	0.9963		
1π					0.9947	-0.0982
2π					0.1061	0.9947

TABLE AII. Overlap matrix between CF* and CO. Total shakeup intensity: $I_{\text{tot}}=0.082$ (8.2%). $\pi^* \leftarrow \pi$ shakeup intensity: $I_{\pi^* \leftarrow \pi}=0.036$ (3.6%). Those parts of the overlap matrices constructed from occupied orbitals are enclosed by bold lines.

CO \ CF*	3σ	4σ	5σ	6σ	1π	2π
3σ	0.9973	0.0682	0.0090	0.0217		
4σ	-0.0652	0.9835	0.1671	0.0202		
5σ	0.0227	-0.1670	0.9832	-0.0686		
6σ	-0.0215	0.0070	0.0713	0.9972		
1π					0.9806	-0.1957
2π					0.1957	0.9806

TABLE AIII. Overlap matrix between NO* and N₂. Total shakeup intensity: $I_{\text{tot}}=0.073$ (7.3%). $\pi^* \leftarrow \pi$ shakeup intensity: $I_{\pi^* \leftarrow \pi}=0.027$ (2.7%). Those parts of the overlap matrices constructed from occupied orbitals are enclosed by bold lines.

N ₂ \ NO*	3σ	4σ	5σ	6σ	1π	2π
3σ	0.9891	0.1378	0.0482	0.0209		
4σ	-0.1234	0.9658	0.2279	0.0020		
5σ	0.0788	-0.2193	0.9717	-0.0396		
6σ	-0.0174	0.0286	0.0390	0.9990		
1π					0.9846	-0.1744
2π					0.1744	0.9846

TABLE BI. Wave function symmetries for ground and excited states for neutral and core ionized diatomic molecules.

	Primary holestate	$\sigma \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\sigma \rightarrow \sigma^*$
	conf. $(3\sigma_u^2)(1\pi_u^4)$	$(3\sigma_u^4)(1\pi_u^4)(3\sigma_g^4)$	$(3\sigma_u^2)(1\pi_u^3)(1\pi_g^1)$	$(3\sigma_u^4)(1\pi_u^4)(3\pi_g^1)$
N ₂	neutral $^1\Sigma_g^+$	$1,3\Pi_g$	$1,3\Sigma_u^+, 1,3\Sigma_u^-, 1,3\Delta_u$	$1,3\Sigma^+$
	1s hole $^2\Sigma_{g,u}^+$	$^2\Pi_{g,u}(2); ^4\Pi_{g,u}$	$^2\Sigma_{g,u}^+(2); ^4\Sigma_{g,u}^+$ $^2\Sigma_{g,u}^-(2); ^4\Sigma_{g,u}^-; ^2\Delta_{g,u}(2); ^4\Delta_{g,u}$	$^2\Sigma_{g,u}^+(2); ^4\Sigma_{g,u}^+$
	conf. $(1\pi^4)(5\sigma^2)$	$(1\pi^4)(5\sigma^1)(2\pi^1)$	$(1\pi^3)(5\sigma^2)(2\pi^1)$	$(1\pi^4)(5\sigma^1)(6\sigma^1)$
CO	neutral $^1\Sigma^+$	$1,3\pi$	$1,3\Sigma^+, 1,3\Sigma^-, 1,3\Delta$	$1,3\Sigma^+$
	1s hole $^2\Sigma^+(2)$	$^2\Pi(2); ^4\Pi$	$^2\Sigma^+(2); ^4\Sigma^+$ $^2\Sigma^-(2); ^4\Sigma^-; ^2\Sigma(2); ^4\Delta$	$^2\Sigma^+(2); ^4\Sigma^+$
	conf. $(1\pi^4)(5\sigma^2)(2\pi^1)$	$(1\pi^4)(5\sigma^1)(2\pi^2)$	$(1\pi^3)(5\sigma^2)(2\pi^2)$	$(1\pi^4)(5\sigma^1)(2\pi^1)(6\sigma^1)$
NO	neutral $^2\Pi$	$2,4\Sigma^+; 2,4\Sigma^-; ^2\Delta$	$^2\Pi; ^4,2\Pi_g; ^2\Pi_i; ^2\Phi_g$	$^2\Pi(2); ^4\Pi$
	1s hole $1,3\Pi$	$1,3\Sigma^+; 1,5\Sigma^-; ^3\Sigma^-(2); 1,3\Delta$	$^1\Pi(3); ^3\Pi_i(2); ^3\Pi_g(2)$ $^5\Pi; 1,3\Phi$	$^1\Pi(2); ^3\Pi(3); ^5\Pi$
	conf. $(3\sigma_u^2)(1\pi_u^4)(1\pi_g^2)$	$(3\sigma_u^4)(1\pi_u^4)(1\pi_g^2)$	$(3\sigma_u^2)(1\pi_u^3)(1\pi_g^2)$	$(3\sigma_u^4)(1\pi_u^4)(1\pi_g^2)(3\sigma_g^1)$
O ₂	neutral $^2\Sigma_g^-$	$1,3\Pi_u$	$1,3\Sigma_u^+; 1,3\Sigma_u^-; 1,3\Delta_u$	$1,3\Sigma_u^+; 1,5\Sigma_u^-; 1,3\Delta_u; ^3\Sigma_{g,u}^-(2)$
	1s hole $^2,4\Sigma_{g,u}^-$	$^2\Pi_{g,u}(2); ^4\Pi_{g,u}$	$^2\Sigma_{g,u}^+(2); ^4\Sigma_{g,u}^+; ^2\Sigma_{g,u}^-(2)$ $^4\Sigma_{g,u}^-; ^2\Delta(2); ^4\Delta$	$^2\Sigma_{g,u}^+(2); ^2\Sigma_{g,u}^-(3); ^2\Delta_{g,u}(2)$ $^4\Sigma_{g,u}^+; ^4\Sigma_{g,u}^-(3); ^4\Delta_{g,u}; ^6\Sigma_{g,u}^-$

	HOMO NUCLEAR	HETERO NUCLEAR
σ^*	3 σ_u	6 σ
π^*	1 π_g	2 π
π	1 π_u	1 π
σ	3 σ_g	5 σ

FIG. 7. One electron orbital scheme of the outermost levels of a diatomic molecule. Indicated on the right are the symmetries for a diatomic with and without inversion symmetry, assuming both atoms are from the first row of the periodic table.

APPENDIX B

According to Herzberg⁴⁴ a general orbital scheme for diatomics is given in Fig. 7. The relative ordering of the low lying π and σ levels varies from molecule to molecule. The ground state and lowest excited valence electron configurations are given in Table BI for each molecule which is independent of the orbital ordering. The spectroscopic states with and without the presence of a 1s core hole are given. Applying the selection rule given in Eq. (4), only those $2p-h$ states are observed which have the same symmetry as the primary hole state. The states which are marked satisfy this rule. The corresponding states in the neutral are used for the comparison in Fig. 5.

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